Indian J. Phys. **79** (1), 47-50 (2005)

AN INTERNATIONAL JOURNAL IJP

Relationship between isothermal bulk modulus and volume expansion ratio for ionic solids

S K Srivastava*

Department of Physics, Jind Institute of Engg and Technology, Jind-126 102, Haryana, India

E-mail : sanjeevsrivastava1980@rediffmail.com

Received 15 March 2003, accepted 10 November 2004

Abstract : In the present study, the different relationships between K_T and (V/V_0) for ionic solids *viz* NaCl, KCl, MgO and CaO have been analyzed. The analysis is based on the experimental data reported by Anderson and extrapolated by Singh and Chauhan. It is found that the relationship $\ln K_T = B(V/V_0)$ + constant, may be used to understand the thermoelastic behaviour of solids assuming that the isothermal bulk modulus varies linearly with temperature. The present communication reveals that the Anderson- Gruneisen parameter increases with temperature

Keywords : Isothermal Bulk Modulus, Volume Thermal Expansion, Ionic Solids.

PACS No. : 62 20.Dc

1. Introduction

Many workers [1-6] have made various efforts to exploit thermodynamic properties of solids under the effect of high temperatures because they are of fundamental interests to geophysical and geochemical theories of interior of the earth [7]. It is known that adequate knowledge of temperature-dependence of bulk modulus (K_T) is necessary for understanding of the thermodynamic and anharmonic properties of the crystal [8]. The volume-temperature relationship and the data on thermal expansivity are required for investigating the equation of state and predicting the compression data of solids at high temperatures [9,10].

The volume thermal expansion coefficient is defined as

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P \tag{1}$$

and the isothermal bulk modulus is written as

$$K_T = -V\left(\frac{dP}{dV}\right)_T . \tag{2}$$

Permanent Address : 4525, Defence Colony, Jind-126 102, Haryana, India.

One of the important parameters in high temperatures physics, which is used to understand the thermodynamic and thermoelastic behaviour of solids is the Anderson-Gruneisen parameter. This parameter is defined as follows

$$\delta_T = \frac{1}{\alpha K_T}\left(\frac{dK_T}{dT}\right)_P . \tag{3}$$

Eq. (1) may be arranged in the following form

$$\frac{dV}{V} = \int \alpha dT \tag{4}$$

and eq.(3) may be written as

$$\frac{dK_T}{K_T} = -\delta_T \int \alpha dT . \tag{5}$$

Solving eq.(4) along with eq.(5), we get the relationship

$$\left(\frac{K_T}{K_0}\right) = \left(\frac{V}{V_0}\right)^{-\delta_T} . \tag{6}$$

Logarithmic of eq.(6) yields

$$\ln K_T = -\delta_T \ln\left(\frac{V}{V_0}\right) + \text{ constant.} \tag{7}$$

In the present work, an attempt has been made to find an exact relationship between isothermal bulk modulus and volume expansion ratio. The method of analysis is shown in Section 2 and the results are discussed in Section 3.

2. Method of analysis

Eq.(7) represents a simple relationship between K_T and volume expansion ratio, (V/V_0). However, relationship (7) is derived using an approximation *i.e.* the Anderson-Gruneisen parameter does not vary with temperatures. The experimental data reported by Anderson [11] show that δ_T is not strictly constant with temperatures. Thus to find an exact relationship between K_T and (V/V_0), an attempt has been made to plot ln K_T *versus* ln(V/V_0), ln K_T *versus* (V/V_0) and K_T *versus* (V/V_0) taking the experimental data reported by Anderson [11] and extrapolated data reported by Singh and Chauhan [12] for ionic solids. The ionic solids which are considered here, are NaCl, KCl, MgO and CaO. Since the plots are of similar nature for different solids, these are shown only in case of MgO in Figures 1 and 2. It is found that plots reveal almost straight lines for ln K_T *versus* (V/V_0) and ln K_T *versus* (V/V_0) but show nonlinear nature for K_T *versus* (V/V_0), resulting following relationships :

$$\ln K_T = A \ln\left(\frac{V}{V_0}\right) + \text{constant}, \tag{8}$$

$$\ln K_T = B\left(\frac{V}{V_0}\right) + \text{constant}, \tag{9}$$

where A and B are constants which can be measured from corresponding plots. Differentiation of eqs. (8) and (9) with respect to temperature T along isobaric condition, yields

$$\frac{1}{K_T}\left(\frac{dK_T}{dT}\right) = \frac{A}{V}\left(\frac{dV}{dT}\right) \text{ and} \tag{10}$$

$$\frac{1}{K_T}\left(\frac{dK_T}{dT}\right) = \frac{B}{V_0}\left(\frac{dV}{dT}\right). \tag{11}$$

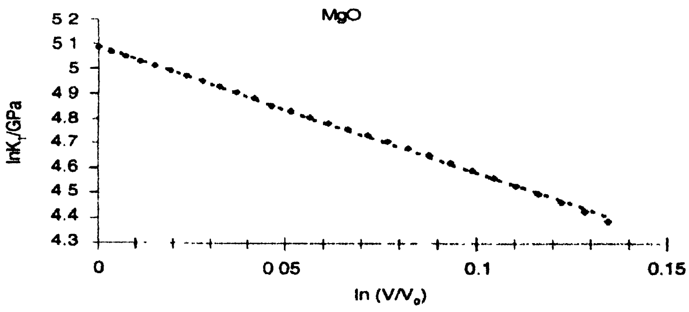
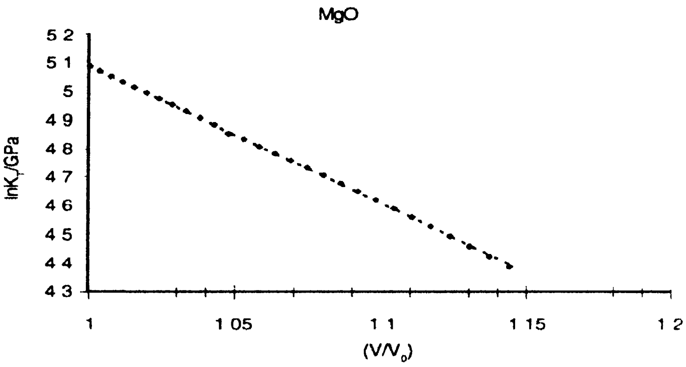


Figure 1. Plot of $\ln[K_T/GPa]$ *versus* $\ln\left(\frac{V}{V_0}\right)$.

After simplifications and using eq.(1), we get following relationship corresponding to eqs.(10) and (11)

$$\left(\frac{dK_T}{dT}\right) = A\alpha K_T, \tag{12}$$

$$\left(\frac{dK_T}{dT}\right) = B\alpha K_T\left(\frac{V}{V_0}\right). \tag{13}$$



Figures 2. Plot of $\ln[K_T/GPa]$ *versus* $\left(\frac{V}{V_0}\right)$

3. Results and discussion

It is found [12-14] that the isothermal bulk modulus varies linearly with temperatures starting from room temperature. Thus, we may write

$$\left(\frac{dK_T}{dT}\right) = \text{constant}. \tag{14}$$

Applying the above condition to eqs.(12) and (13), we get following relationships:

$$\alpha K_T = \text{constant}, \tag{15}$$

$$\alpha K_T\left(\frac{V}{V_0}\right) = \text{constant}. \tag{16}$$

Taking the experimental data reported by Anderson [11] and extrapolated by Singh and Chauhan [12], the values of αK_T and $\alpha K_T(V/V_0)$ have been calculated for NaCl, KCl, MgO and CaO. The calculated values are shown in Tables 1-4. It is found that the product αK_T does not remain strictly constant. At very high temperatures, as the temperature increases, the product αK_T decreases continuously and significantly. This is mainly because the variation of α with T in high temperature domain deviates significantly from the linearity, which is evident from the experimental studies [15-17]. The prediction that αK_T decreases slowly with temperatures at high temperatures, is consistent with the recent studies [18,19]. The variation of αK_T

with temperatures reveals the invalidity of relationship represented by eq.(8).

Table 1. Calculated values of $\alpha K_T (10^{-4} K^{-1} GPa)$, $\alpha K_T \frac{V}{V_0} (10^{-4} K^{-1} GPa)$, and δ_T for NaCl.

T(K)	$\alpha(10^{-5}K^{-1})$	$K_T(GPa)$	(V/V_0)	αK_T	$\alpha K_T (V/V_0)$	δ_T	δ_T [11]
300	11.8	24.0	1.0000	28.32	28.32	5.56	5.56
350	12.2	23.2	1.0061	28.30	28.48	5.56	5.62
400	12.7	22.4	1.0127	28.45	28.81	5.53	5.69
450	13.2	21.6	1.0194	28.51	29.07	5.52	5.74
500	13.7	20.8	1.0261	28.50	29.24	5.53	5.82
550	14.3	19.9	1.0335	28.46	29.41	5.53	5.95
600	14.8	19.0	1.0410	28.12	29.27	5.60	6.10
650	15.4	18.1	1.0486	27.87	29.23	5.65	6.24
700	16.0	17.3	1.0568	27.68	29.25	5.69	6.37
750	16.6	16.5	1.0657	27.39	29.19	5.75	6.53
800	17.0	15.7	1.0747	26.69	28.68	5.90	
850	17.6	14.8	1.0841	26.05	28.24	6.04	
900	18.1	14.0	1.0938	25.34	27.72	6.21	
950	18.6	13.2	1.1038	24.55	27.10	6.41	
1000	19.1	12.3	1.1143	23.49	26.18	6.70	
1050	19.6	11.5	1.1251	22.54	25.36	6.99	

Table 2. Calculated values of $\alpha K_T (10^{-4} K^{-1} GPa)$, $\alpha K_T \frac{V}{V_0} (10^{-4} K^{-1} GPa)$, and δ_T for KCl.

T(K)	$\alpha(10^{-5}K^{-1})$	$K_T(GPa)$	(V/V_0)	αK_T	$\alpha K_T (V/V_0)$	δ_T	δ_T [11]
300	11.0	17.0	1.0000	18.70	18.70	5.84	5.84
350	11.3	16.4	1.0056	18.53	18.64	5.89	5.88
400	11.7	15.9	1.0117	18.60	18.82	5.87	5.88
450	12.1	15.4	1.0175	18.63	18.96	5.86	5.88
500	12.6	14.7	1.0243	18.52	18.97	5.90	5.88
550	13.2	14.2	1.0307	18.74	19.32	5.83	5.87
600	13.7	13.7	1.0377	18.77	19.48	5.82	5.84
650	14.2	13.2	1.0448	18.74	19.58	5.83	5.83
700	14.7	12.6	1.0526	18.52	19.50	5.90	5.90
750	15.2	12.0	1.0605	18.24	19.34	5.99	5.98
800	15.7	11.5	1.0685	18.06	19.29	6.05	6.04
850	16.2	10.9	1.0772	17.66	19.02	6.18	6.19
900	16.7	10.3	1.0867	17.20	18.69	6.35	
950	17.2	9.8	1.0960	16.86	18.47	6.48	
1000	17.7	9.3	1.1056	16.28	18.00	6.71	

Table 3. Calculated values of $\alpha K_T (10^{-4} K^{-1} GPa)$, $\alpha K_T \frac{V}{V_0} (10^{-4} K^{-1} GPa)$, and δ_T for MgO

T(K)	$\alpha(10^{-5}K^{-1})$	$K_T(GPa)$	(V/V_0)	αK_T	$\alpha K_T (V/V_0)$	δ_T	δ_T [11]
300	3.12	161.6	1.0000	50.42	50.42	5.26	5.26
400	3.57	158.9	1.0034	56.73	56.92	4.68	4.83
500	3.84	156.1	1.0073	59.94	60.38	4.42	4.69
600	4.02	153.2	1.0113	61.59	62.28	4.31	4.67
700	4.14	150.4	1.0153	62.27	63.22	4.26	4.70
800	4.26	147.4	1.0196	62.79	64.02	4.22	4.74
900	4.38	144.3	1.0240	63.20	64.72	4.20	4.78
1000	4.47	141.4	1.0284	63.21	65.00	4.20	4.84
1100	4.56	138.3	1.0331	63.06	65.15	4.21	4.92
1200	4.65	135.1	1.0379	62.82	65.20	4.22	4.99
1300	4.71	132.1	1.0428	62.22	64.88	4.26	5.08
1400	4.80	128.1	1.0476	61.49	64.41	4.31	5.12
1500	4.89	125.7	1.0529	61.47	64.72	4.31	5.13
1600	4.98	122.5	1.0582	61.01	64.56	4.35	5.07
1700	5.04	119.6	1.0635	60.28	64.11	4.40	4.95
1800	5.13	116.6	1.0689	59.82	63.94	4.43	4.66
1900	5.24	113.7	1.0745	59.58	64.02	4.45	
2000	5.32	110.7	1.0801	58.89	63.61	4.50	
2100	5.41	107.7	1.0860	58.27	63.28	4.55	
2200	5.50	104.7	1.0919	57.59	62.88	4.61	
2300	5.58	101.7	1.0980	56.75	62.31	4.67	
2400	5.67	98.7	1.1042	55.96	61.79	4.74	
2500	5.75	95.7	1.1105	55.03	61.11	4.82	
2600	5.84	92.7	1.1169	54.14	60.47	4.90	
2700	5.93	89.7	1.1235	53.19	59.76	4.99	
2800	6.01	86.7	1.1302	52.11	58.89	5.09	
2900	6.10	83.7	1.1371	51.06	58.06	5.19	
3000	6.18	80.7	1.1441	49.87	57.06	5.32	

Wang and Reeber [18] have found that the product $\alpha K_T V$ (and not αK_T) approaches a constant value at high temperatures. This finding is based on a modified Einstein model applied to different materials [18,20]. It is seen from Tables 1-4 that $\alpha K_T (V/V_0)$ for the ionic solids under study, remains constant up to a greater extent than αK_T for the whole range of temperatures. The physical significance of the prediction that $\alpha K_T V$ is nearly constant, has been provided by Wang and Reeber [18] on the basis of the variation of thermal pressure (P_{TH}) with temperature. They have expressed $\alpha K_T V$ as the partial temperature derivative of work done by the thermal

Table 4. Calculated values of $\alpha K_T (10^{-4} K^{-1} GPa)$, $\alpha K_T \frac{V}{V_0} (10^{-4} K^{-1} GPa)$, and δ_T for CaO

T(K)	$\alpha(10^{-5} K^{-1})$	$K_T(GPa)$	(V/V_0)	αK_T	$\alpha K_T (V/V_0)$	δ_T	δ_T [11]
300	3 04	110.6	1 0000	33 62	33 62	6.19	6.19
400	3 47	108 5	1 0033	37.65	37 77	5 53	5 54
500	3 67	106 4	1.0066	39 05	39 31	5 33	5 27
600	3 81	104 3	1 0106	39 74	40 16	5.24	5 14
700	3 92	102 3	1 0145	40 10	40 68	5.19	5.07
800	4 01	100.3	1 0186	40 22	40 97	5 17	5 03
900	4 08	98 4	1 0226	40 15	41 05	5 18	5 01
1000	4 14	96 3	1 0267	39 87	40.93	5.22	5 00
1100	4 20	94 3	1.0311	39 61	40.84	5.25	5.01
1200	4 26	92.3	1 0356	39 32	40 72	5 29	5 01
1300	4 36	90.3	1 0401	39 37	40.95	5.29	
1400	4.43	88.3	1.0446	39.12	40.86	5.32	
1500	4 50	86 3	1.0493	38 84	40.75	5.36	
1600	4.58	84.2	1.0541	38.56	40.65	5 40	
1700	4 65	82.2	1.0590	38.22	40 48	5.44	
1800	4.72	80.2	1.0639	37.85	40.27	5.50	
1900	4.80	78.1	1.0690	37.49	40.07	5.55	
2000	4.87	76.1	1.0742	37.06	39.81	5.62	
2100	4.94	74 1	1 0795	36.61	39 52	5.69	
2200	5 01	72 1	1 0849	36 12	39.19	5.76	
2300	5.09	70.0	1.0904	35 63	38.85	5.84	
2400	5 16	68 0	1.0960	35 09	38.46	5.93	
2500	5.23	66.0	1.1017	34.52	38.03	6.03	
2600	5 31	64.0	1.1075	33 98	37.64	6.12	
2700	5 38	62.0	1.1134	33.36	37 14	6.24	
2800	5.45	59.9	1.1195	32 65	36.55	6.37	

would imply that the work done $(P_{TH} V)$ changes linearly with temperature. This prediction reinforces the validity of the relationship between isothermal bulk modulus and volume expansion ratio in the form of eq. (9).

If the relationship given by eq.(14) is strictly true, then using eq.(3), we get the following relationship for temperature dependence of the Anderson-Gruneisen parameter

$$\delta_T = \delta_T^0 \frac{\alpha_0 K_0}{\alpha K_T} \tag{17}$$

Here, δ_T^0 is the value of the Anderson- Gruneisen parameter at 300K. The value of δ_T^0 for ionic solids is extracted from those reported by Anderson [11]. The predicted values of δ_T at different temperatures using eq.(17) are listed in Tables 1-4 for corresponding solids along with the values of δ_T predicted by Anderson [11]. The present study shows that the value of δ_T increases with temperature in high temperature region.

Hence in the present study, the different relationships between K_T and (V/V_0) have been analyzed for ionic solids *viz.* NaCl ,KCl ,MgO and CaO. It is found that the relationship given by eq.(9) may be used to understand the thermodynamic and thermoelastic behaviour of solids with temperatures. However, the present work is based on the fact that the isothermal bulk modulus varies linearly with temperature.

Acknowlegments

The author is thankful to the referee for his valuable comments, which have been used in revising the manuscript. Thanks are also due to Prof. Jai Shanker of Dr B.R.Ambedkar University, Agra for some useful discussions.

References

[1] A M Sherry and M Kumar *J Phys Chem Sol* **52** 1145 (1991)
[2] J L Tollon *J Phys Chem Sol* **41** 837 (1980)
[3] M P Verma and B Dayal *Phys Stat. Sol* **(b) 3** 901 (1963)
[4] M Kumar and S P Upadhyaya *Phys. Stat. Sol.* **(b) 181** 55 (1994)
[5] M Kumar *Physica* **B205** 175 (1995)
[6] R K Pandey *J. Phys. Chem Sol.* **59** 1157 (1998)
[7] O L Anderson, D G Isaak and H Oda *Rev Geophys.* **3** 57 (1992)
[8] Q He and Z T Yan *Phys. Stat. Sol.* **(b) 223** 767 (2001)
[9] R Boehler and G C Kennedy *J Phys. Chem. Sol* **41** 517,1019 (1980)
[10] T G Plymate and J H Stout *J. Geophys Res* **B94** 9477 (1989)
[11] O L Anderson *Equations of State of Solids for Geophysics and Ceramic Science* (Oxford· Oxford University Press) (1995)
[12] K S Singh and R S Chauhan *Physica* **B** 315 74 (2002)
[13] V Pal , M Kumar and B R K Gupta *Phys. Chem. Miner.* **25** 227 (1998)
[14] S S Kushwah and J Shanker *High Temperatures - High Pressures* **27** 177 (1995)
[15] L S Dubrovinskey and S K Saxena *Phys. Chem. Miner* **24** 547 (1997)
[16] GFiquet, P Richet and G Montagnae *Phys. Chem. Miner.* **27** 103 (1999)
[17] M H G Jacobs and H A J Oonk *Phys. Chem. Chem. Phys* **2** 2641 (2002)
[18] K Wang and R R Reeber *J. Mater. Res.* **11** 7 (1996)
[19] M Taravillo,V G Baonza, J E F Rubio, J Nunez and M Cacers *J. Phys. Chem Sol.* **63** 1705 (2002)
[20] K Wang and R R Reeber *J. Phys. Chem. Sol.* **56** 7 895 (1995)